



High-Voltage Poling of a Bulk Sample of Disperse Red 1 Polymethylmethacrylate Guest-Host Polymer for U.S. Army Electro-Optical Applications

**by Robert H. Lambeth, Adam M. Rawlett, Joshua A. Orlicki,
Joseph M. Dougherty, Nicole E. Zander, Jan Andzelm,
George R. Martin, Robert C. Hoffman, Timothy Pritchett,
Andrew G. Mott, Geoffrey A. Lindsay, Matthew C. Davis,
Stephen Fallis, Andrew P. Chafin, Warren Herman,
and Dong Park**

ARL-TR-4864

July 2009

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

ARL-TR-4864**July 2009**

High-Voltage Poling of a Bulk Sample of Disperse Red 1 Polymethylmethacrylate Guest-Host Polymer for U.S. Army Electro-Optical Applications

**Robert H. Lambeth, Adam M. Rawlett, Joshua A. Orlicki,
Joseph M. Dougherty, Nicole E. Zander, Jan Andzelm,
and George R. Martin
Weapons and Materials Research Directorate, ARL**

**Robert C. Hoffman,
Timothy Pritchett, and Andrew G. Mott
Sensors and Electron Devices Directorate, ARL**

**Geoffrey A. Lindsay, Matthew C. Davis, Stephen Fallis,
and Andrew P. Chafin
Naval Air Warfare Center Weapons Division**

**Warren Herman and Dong Park
University of Maryland, College Park**

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) July 2009		2. REPORT TYPE Final		3. DATES COVERED (From - To) January 2007–November 2008	
4. title and subtitle High-Voltage Poling of a Bulk Sample of Disperse Red 1 Polymethylmethacrylate Guest-Host Polymer for U.S. Army Electro-Optical Applications			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Robert H. Lambeth, Adam M. Rawlett, Joshua A. Orlicki, Joseph M. Dougherty, Nicole E. Zander, Jan Andzelm, George R. Martin, Robert C. Hoffman, Timothy Pritchett, Andrew G. Mott, Geoffrey A. Lindsay, * Matthew C. Davis, * Stephen Fallis, * Andrew P. Chafin, * Warren Herman, † and Dong Park †			5d. PROJECT NUMBER H16		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WMM-A Aberdeen Proving Ground, MD 21005-5069			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-4864		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES *Naval Air Warfare Center Weapons Division, MS 6303, Bldg. 5, 1900 Knox Rd., China Lake, CA 93555 †Laboratory for Physical Sciences, University of Maryland, 8050 Greenmeade Dr., College Park, MD 20740					
14. ABSTRACT The U.S. Army Research Laboratory is currently developing novel materials with high-bulk electro-optic (EO) activities that are transparent in the visible and/or near infrared regions of the spectrum. This multidefense laboratory collaboration is a highly interactive and multispectral research effort (with expertise spanning from molecular modeling, materials development and processing, and system fabrication and testing), which is operating toward the development of fast EO shutters. A computational effort to predict desired physical properties of EO chromophores such as their hyperpolarizability and visible wavelength transparency has been developed. This effort allows the chemists to more efficiently synthesize highly active chromophores within desired specifications. Recently, the team demonstrated the ability to align molecules in a thick polymer film, which is required for a fast protective shutter. EO coefficients comparable to thin film samples have already been measured, with the prospect that bulk values may exceed those for thin films. This development will enable a new class of ultrafast optical devices using the linear EO effect that will operate on a subnanosecond time scale.					
15. SUBJECT TERMS ROMP, electro-optical polymers, bulk poling					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON Robert H. Lambeth
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-306-0281

Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Experimental	3
2.1 Materials	3
2.2 Representative Polymerization Procedure.....	4
2.3 Sample Preparation.....	4
2.4 Instrumentation and Poling Procedure	4
3. Results and Discussion	5
3.1 Bulk Poling of DR1-PMMA Bulk Slab	5
3.2 Tunable High Glass Transition Electro-Optical Polymers by Ring-Opening Metathesis Polymerization	7
4. Conclusions	9
5. References	10
Distribution List	11

List of Figures

Figure 1. Standard and required poling orientations for EO materials.	1
Figure 2. Schematic of proposed solution for fabricating large-aperture devices.	2
Figure 3. Electrode/sample configuration for poling bulk guest-host polymers.	4
Figure 4. Poling-induced birefringence of 10% DR1-PMMA 700- μm slab.	5
Figure 5. Maker fringe experiment to measure SHG d -coefficient.	6
Figure 6. Maker fringe fit of X % DR1-PMMA sample.....	7
Figure 7. Chemical structures of monomers and the catalyst used in this study.	8

List of Tables

Table 1. Thermal data for EO polymers prepared by ROMP.	9
--	---

Acknowledgments

The authors would like to thank Kim Olver for her help in preparing the samples, and Wei Zhang and Ron Moffitt of the Advanced and Applied Polymer Processing Institute in Danville, VA.

INTENTIONALLY LEFT BLANK.

1. Introduction

In recent years, much attention has been paid to poling thin-film doped polymers for electro-optic (EO) applications, mostly in the area of telecommunications switching devices. However, there are applications where a larger thickness of guest-host polymer results in enhanced performance of the EO device, such as in terahertz (THz) generation (1, 2). The thicker path length available in bulk-poled polymers will allow for improved THz power, sensitivity, and signal-to-noise ratio in both THz generators and detectors. Large-area Pockels cells constructed from EO guest-host polymers are used as high-speed modulators and shutters; any application requiring a large d_{33} or r_{33} will potentially benefit from bulk-poled guest-host polymer systems. For large-aperture applications, the optical path length is longer, and both poling and operating fields must still be transverse to the direction of light propagation, which presents a tremendous challenge in building devices (figure 1). Given the limitations of thin-film poling for fabricating large-aperture devices, fabricating a thick EO polymer slab with the proper orientation is an important goal. A proposed solution is to pole a thick slab, cut, polish and reorient 90° (figure 2). A first step toward testing the proposed solution is to describe the fabrication and poling of a 700- μm -thick bulk piece of polymethylmethacrylate (PMMA) doped with various concentrations of Disperse Red 1 (DR1). Maker fringe analysis will demonstrate that under the poling fields currently available (57–71 V/ μm), substantial ordering of the DR1 chromophores is occurring, resulting in birefringence and significant d_{33} and r_{33} values. In an effort to further improve the EO response of the model bulk DR1 system, the synthesis and thermal characterization of covalently attached DR1 to a tunable high glass transition temperature (T_g) polymeric backbone prepared by ring opening metathesis polymerization (ROMP) are described.

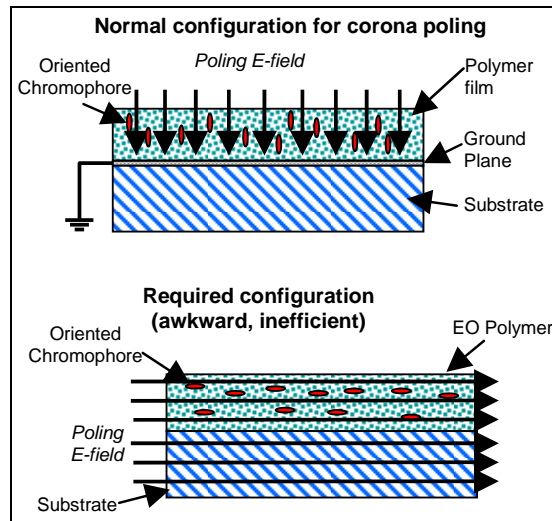


Figure 1. Standard and required poling orientations for EO materials.

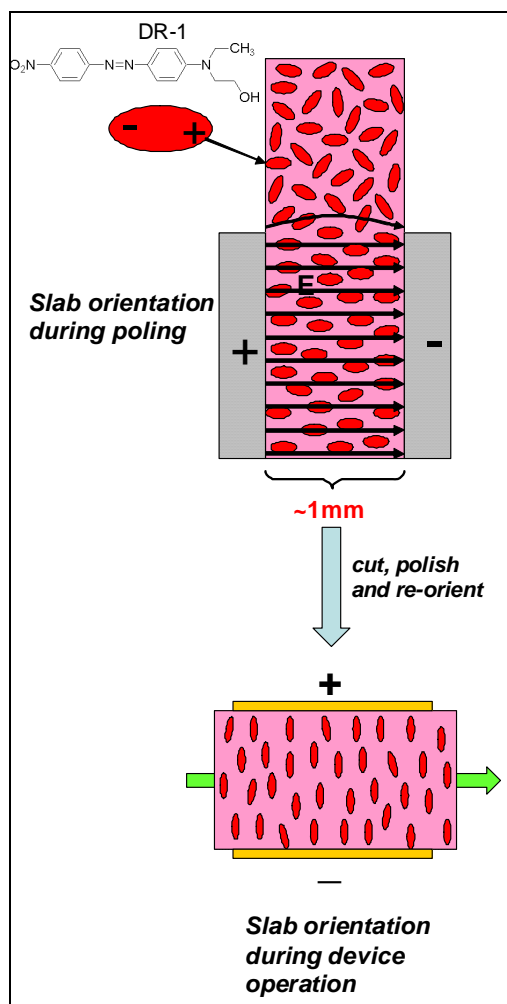


Figure 2. Schematic of proposed solution for fabricating large-aperture devices.

This multidefense laboratory collaboration is a highly interactive and multispectral research effort from molecular modeling, materials development, and system testing. A robust computational effort to predict desired physical properties of EO chromophores, such as their EO coefficient and desired wavelength characteristics, has been developed. The computational efforts can predict both chromophore spectral wavelength characteristics within 30 nm and EO performance trends (3). This effort allows the chemists to more efficiently synthesize highly active chromophores within desired specifications. Numerous chromophores have been synthesized and formulated into polymeric systems via guest-host methodology or directly attaching the chromophore to the polymer. Via ROMP, desired chromophores can be attached to a myriad of polymers, and T_g 's, molecular weight, and other processing properties of the final polymeric materials can be controlled.

2. Experimental

2.1 Materials

All solvents and reagents were purchased from Aldrich and used as-received unless otherwise noted. Compounds **2**, **3**, **4** and 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) were prepared according to the literature. ^1H NMR and ^{13}C NMR data were recorded on a Bruker 600 MHz instrument. All chemical shifts are reported in parts per million (ppm) relative to residual CHCl_3 . Coupling constants (J) are expressed in hertz (Hz). The molecular weight and polydispersity of the polymers were estimated in tetrahydrofuran (THF) at room temperature with a Waters 515 high-performance liquid chromatography pump. The DR1 chromophore was recrystallized from THF. Polymer guest-host systems were prepared by two different methods: (1) coprecipitation of the DR1 and PMMA from THF followed by extrusion and (2) by the microcompounder extrusion method.

The coprecipitation method involves the precipitation of the DR1 chromophore and the PMMA simultaneously from solution. The precipitates are then dried in an oven to remove traces of solvent or moisture that could adversely impact the dielectric breakdown properties of the guest-host polymer. This is followed by compression molding into a thick polymer slab that has smooth surfaces on both sides, allowing for convenient optical measurements.

The microcompounder method begins with the macroscopic mixing of PMMA and the chosen chromophore. This was accomplished by using a vortex mixer or some other high-energy agitation. A DSM Xplore Micro-Compounder was used to perform the physical compounding tasks. A macroscopically mixed polymer blend was charged to the hopper and fed into the extruder. The extruder was fitted with two conical corotating screws and also possessed a recycle loop, allowing melt to recirculate through the system automatically. The general processing conditions consisted of the following: the screw rotation rate was 100 rpm, the barrel temperature was 250 °C, and the processing cycle was ~10 min. A 16-g premixed polymer charge resulted in ~13–15 g of polymer. The remainder of the mixed polymer adhered to screw or barrel.

Norbornyl-DR1 monomer (1). 5-norbornene-2-carboxylic acid (2.02 g, 15.94 mmol), DR1 (5.51 g, 17.52 mmol), and DPTS (0.50 g, 1.59 mmol) were dissolved in CH_2Cl_2 (100 mL) and cooled in an ice bath. In a separate flask, dicyclohexylcarbodiimide (DCC) (3.94 g, 19.12 mmol) was dissolved in CH_2Cl_2 (25 mL) and transferred via cannula to the mixture. The reaction mixture was allowed to gradually warm to room temperature and stir overnight (~18 h). The reaction mixture was vacuum filtered to remove dicyclohexylurea (DCU) and concentrated by rotary evaporation. The crude mixture was dissolved in ethyl acetate (100 mL) and placed in an ice bath for 1 h to crystallize any remaining DCU. Vacuum filtration, concentration, and

recrystallization from ethanol produced the title compound (6.1 g, 88%) as a red solid. Endo-norbornyl isomer: ^1H NMR (600 MHz, CDCl_3): δ 1.27–1.30 (m, 4H), 1.37–1.47 (m, 2H), 1.93 (td, $J = 3.7, 9.4$, 1H), 2.93 (s, 1H), 2.97 (dt, $J = 3.9, 9.4$, 1H), 3.03 (s, 1H), 3.56 (dd, $J = 7.1, 14.3$, 2H), 3.68 (t, $J = 6.3$, 2H), 4.27 (t, $J = 6.3$, 2H), 5.91 (dd, $J = 2.8, 5.6$, 1H), 6.21 (dd, $J = 2.9, 5.6$, 1H), 6.83 (d, $J = 9.1$, 2H), 7.93 (m, 4H), 8.33 (d, $J = 8.8$, 2H) ^{13}C NMR (150 MHz, CDCl_3) δ 12.33, 29.33, 30.47, 41.65, 42.56, 43.11, 43.34, 45.74, 46.42, 46.59, 48.83, 49.72, 61.20, 111.51, 122.67, 124.69, 126.28, 132.20, 135.65, 138.05, 138.17, 143.86, 147.43, 151.33, 156.79, 174.74.

2.2 Representative Polymerization Procedure

A solution of **4** (11.1 mg, 0.013 mmol) in CH_2Cl_2 (1 mL) was rapidly injected via syringe into a vigorously stirred solution of **1** (150 mg, 0.34 mmol), **2** (75 mg, 0.49 mmol), and **3** (275 mg, 0.68 mmol) in CH_2Cl_2 (9 mL) at room temperature. After 30 min, a large excess of ethyl vinyl ether was added to quench the polymerization. The reaction mixture was poured into stirred methanol, and the resulting precipitate was collected by vacuum filtration and dried under high vacuum.

2.3 Sample Preparation

Figure 3 shows a sample prepared by the coprecipitation or microcompounder method ready for poling. The polymer sample is $\sim 2.5\text{ cm} \times 2.5\text{ cm} \times 0.7\text{ mm}$ thick. Two aluminum electrodes fabricated from electron microscopy sample mounts were attached to the polymer sample. The electrodes were polished to allow the electrode intimate contact with the polymer. Methods of attachment included temporary bonding of the aluminum electrode to a 100- to 200-nm vacuum-deposited Au pad with Ag paste, and by simple pressure contact of the aluminum stub against the polymer sample with no Au contact pad.

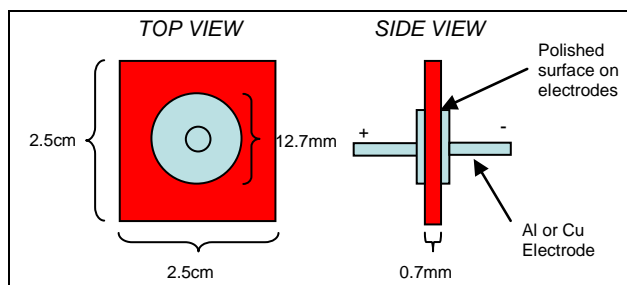


Figure 3. Electrode/sample configuration for poling bulk guest-host polymers.

2.4 Instrumentation and Poling Procedure

A Spellman 100-kV high-voltage DC power supply (Model SL120P60) was used to supply the high voltage required for poling. The sample with attached aluminum electrodes was connected to the power supply and then immersed in silicone oil contained in a Teflon cup. A Teflon cap was placed over the bath to prevent the walls of the oven from arcing. The oven was modified to allow the insulated high-voltage lead to enter through the back of the oven. The entire

bath/sample assembly was then placed in an oven for poling. To accomplish poling, the voltage was increased to 40–50 kV (57–71 V/ μm), and the temperature ramped to 90 °C from ambient (25° C) in ~30 min, followed by a period of poling at 90 °C for 15 min, then followed by a cooldown with forced nitrogen to 25–35 °C over a period of 120–180 min. The high voltage was applied to the sample throughout the entire poling process. When cooled, the voltage was turned off and the sample was removed and gently cleaned of the silicone oil with a mild solution of Alconox detergent. The gold pads were removed either by gentle rubbing or by etching with a solution of aqueous potassium iodide. The samples were stored at ~ -10 °C until measurements were taken.

3. Results and Discussion

3.1 Bulk Poling of DR1-PMMA Bulk Slab

The as-poled polymers were placed on a rotation stage between crossed polarizers to measure their birefringence. Figure 4 clearly indicates that the DR1-PMMA was poled under the conditions described. The birefringence decayed over a period of several days (an expected property of the DR1-PMMA guest-host system).

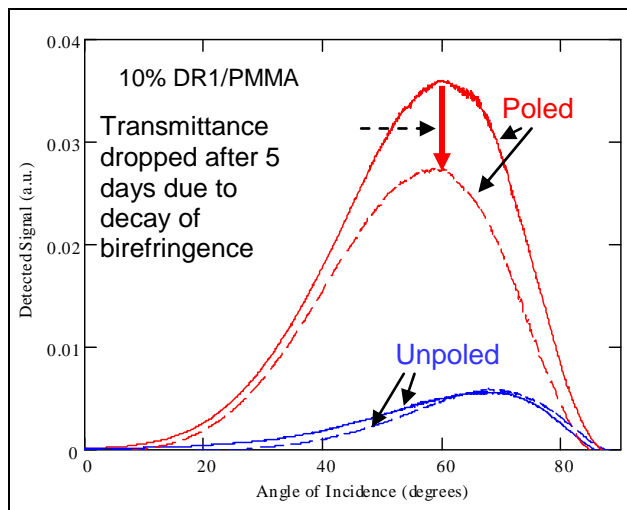


Figure 4. Poling-induced birefringence of 10% DR1-PMMA 700- μm slab.

Further poling confirmation comes from an examination based on a Maker-fringe fit based on an absorbing isotropic medium (4). The apparatus used in the analysis is shown in figure 5.

For observing second-harmonic generation (SHG), the sample was positioned at the waist of a lightly focused (150-mm lens) fundamental beam (1319 nm) produced by a diode-pumped Q-switched Nd: YAG laser. The pulse width was 14 ns and the repetition rate was 750 Hz. The fundamental beam was polarized inside the laser cavity, and a half-wave plate was used to

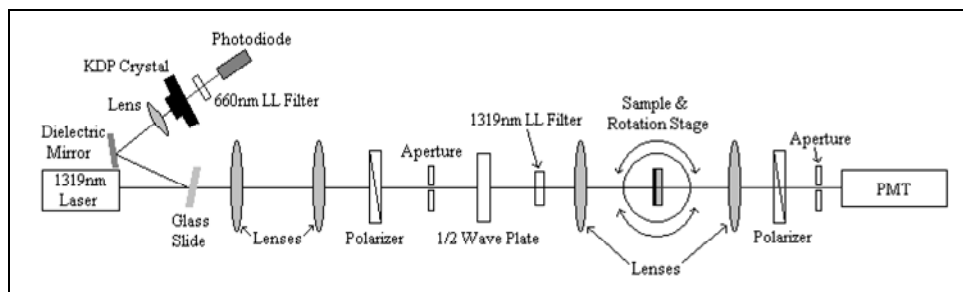


Figure 5. Maker fringe experiment to measure SHG d -coefficient.

control the polarization of the beam incident on the sample. For the following data, the fundamental beam was p-polarized, and a polarizer after the sample was set for detection of the p-polarized component of the SH output. The SHG signal was detected by a Hamamatsu R928 photomultiplier tube in conjunction with a Stanford Research SR250 boxcar averager. To account for laser power fluctuations, part of the fundamental beam was split off and sent through a lithium iodate crystal to produce a reference second harmonic signal. The sample was mounted on a computer-controlled Oriel rotation stage, and data was collected by computer at 1° to 2° increments of the angle of incidence.

Using data from the Maker fringe data at 1319 nm collected on a 10% DR1 coprecipitated sample, the largest measurable d_{33} was an estimated 9 pm/V. In turn, an r_{33} at 1319 nm of 3.7 pm/V was estimated. The λ_{\max} for the DR1-PMMA system is at 478 nm and therefore the value of $r_{33} = 6.1$ pm/V at 810 nm was estimated. This compares favorably with the highest r_{33} observed in a DR1-copolymer system (7.5 pm/V) (5). This sample had an abundance of DR1 precipitates that obscured some of the fine structure in the Maker fringe scan. Subsequent samples (figure 6) were processed with the microcompounder extrusion method that yielded samples with a very smooth surface morphology and many fewer particulates. The 10% DR1 (120D, 120Da, 120Db) samples exhibited high-contrast fringes, while the 15% DR1 (124B, 124Ba) samples showed evidence of precipitates while still having a significantly higher SHG response. Further differences can be seen in the type of electrode used for poling. Sample 124B had gold pads whereas sample 124Ba did not. In this case, the absence of gold electrodes appears to result in an enhancement, while in the 10% DR1 case it does not. This is likely due to polymer processing variables; one can observe color banding due to the variation in absorption of the DR1 in the PMMA matrix. Optical inhomogeneities due to particulates and concentration gradients accumulating at the leading edge of the extruded polymer as it fills the mold can also be observed.

Comparing the first lot of samples that were made of coprecipitated DR1-PMMA material (~ 6 pm/V) with the later lots of microcompounded DR1-PMMA material (< 1 pm/V), it appears that every sample containing particles of DR1 has a higher r_{33} than would normally be expected for such a sample. In addition, there seems to be no clear advantage to using gold pads to assist in the poling process. The problem of precipitates should be avoided by using a copolymer in

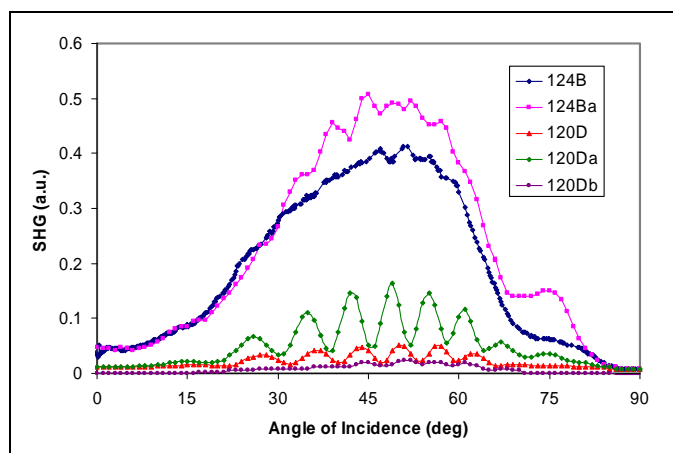


Figure 6. Maker fringe fit of X % DR1-PMMA sample.

which the chromophore is chemically bonded to the polymer host. Furthermore, if it is correct that the gold pads are not necessary for poling, the fabrication of devices will be simplified.

3.2 Tunable High Glass Transition Electro-Optical Polymers by Ring-Opening Metathesis Polymerization

As described previously, there is an interest in poling bulk EO materials for their potential for enhanced THz generation. One of the challenges in preparing materials for practical applications involves preventing decay of the poling-induced polar order for extended periods of time during device operation (6). In the current system, DR1 is doped as a guest in a PMMA matrix. While the initial poling results are promising, the poling-induced order quickly decays with time. This is primarily due to the low T_g of the PMMA matrix. The thermal stability can often be improved by tethering the EO chromophores to high T_g polymer backbones. Many of the materials prepared in this regard are not easily processed (7) and require either demanding reaction conditions unsuitable for the EO chromophore or post-polymerization modification. Thermally stable EO materials were prepared via direct polymerization of chromophore-containing monomers under mild reaction conditions. ROMP is an attractive alternative to other modes of polymerization because well-defined, high-molecular-weight polymers can be obtained under undemanding reaction conditions with excellent functional group tolerance (8). It is anticipated that ROMP will be a viable route to directly produce EO polymers, where the desired chromophore is incompatible with other polymerization methods.

The goal was to copolymerize an EO chromophore-tethered monomer such as **1** with norbornyl-monomers **2** and **3** as a method for preparing polymers with controllable T_g 's. Polymers derived from *exo*-*N*-phenylnorbornenedicarboxamide (**2**) are thermally robust with T_g 's exceeding 200 °C and soluble in common organic solvents. Modifying the feed ratio between monomers **2** and **3** with constant **1** should prepare polymers with predetermined T_g 's, allowing the material to be tuned according to the desired processing conditions.

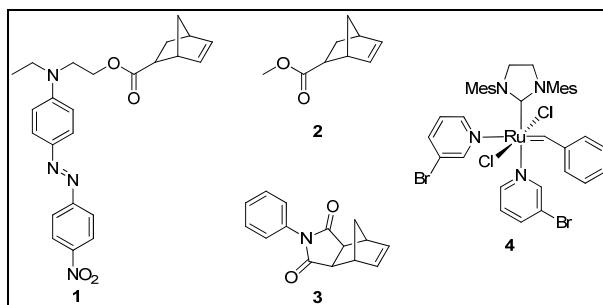


Figure 7. Chemical structures of monomers and the catalyst used in this study.

Commercially available DR1 was used as a model chromophore for this study, which is attached to the polymerizable norbornene unit via DCC/DPTS coupling. Acrylic monomers containing DR1 are difficult to polymerize to high molecular weights by free radical polymerization. It has been shown that similar azobenzene-tethered norbornyl-monomers are readily polymerized in a controlled fashion by complex **4** (9).

Monomers **1**, **2**, and **3** were initially homopolymerized in the presence of complex **4** with target molecular weights of 40 kDa. Five copolymer samples were also prepared with target molecular weights of 40 kDa, where the weight fraction of monomer **1** in the feedstock was held constant at 30% while the ratios of monomers **2** and **3** were varied. Gel permeation chromatography characterization indicated that the polymers were well-defined as evidenced by nearly monomodal peak shapes and low polydispersity indexes (1.1–1.2).

The polymers were characterized by DSC heating from 25–200 °C at 10 °C/min with two heating cycles. The values reported were taken from the second heating scan. The T_g 's of the homopolymers (samples P1–P3) were used to estimate the values of the copolymers (samples P4–P8) using the Fox equation (10) (see table 1).

As anticipated, the T_g of the copolymers increased as the ratio of monomer **2** to **3** was decreased. For a copolymer with 30 weight-percent of monomer **1**, the T_g can be manipulated from 89 to 189 °C simply by varying ratios of **2** and **3** in the monomer feedstock. The polymers are also soluble in a variety of common organic solvents and are easily processed under bulk conditions. These characteristics make ROMP a highly attractive method for preparing EO polymers. Materials that combine high thermal stability and processability were previously difficult to obtain without postpolymerization modification or lattice-hardening procedures during poling. The use of ROMP should simplify the overall process and provide materials capable of realizing higher EO coefficients in the bulk.

Table 1. Thermal data for EO polymers prepared by ROMP.

Sample	Monomer Feedstock			T_g (°C) (calc)	T_g (°C) (DSC)
	W1	W2	W3		
P1	1	0	0	—	103.8
P2	0	1	0	—	78.8
P3	0	0	1	—	234.8
P4	0.3	0.7	0	84.9	89.3
P5	0.3	0.55	0.15	95.1	106.64
P6	0.3	0.35	0.35	113.3	132.9
P7	0.3	0.15	0.55	140.1	163.1
P8	0.3	0	0.7	170.3	189.2

Note: Calculated according to the Fox equation. Value reported is from second heating cycle.

4. Conclusions

This report describes the fabrication and poling of a 700- μm -thick bulk piece of PMMA doped with various concentrations of DR1. Maker fringe analysis demonstrated that under the poling fields currently available (57–71 V/ μm), substantial ordering of the DR1 chromophores is occurring, resulting in birefringence and significant d_{33} and r_{33} values. An estimated value of $r_{33} = 3.7$ pm/V at 1319 nm was measured. The estimated value of r_{33} at 810 nm was 6.1 pm/V. This compares favorably with the highest r_{33} observed in a DR1-copolymer system (7.5 pm/V at 800 nm).

There are currently unresolved issues with regard to the role of precipitates in the poling process, as samples with DR1 particulates had more of a response than would be expected of an EO polymer with particulates. This should be avoided by switching to a chromophore-host copolymer in which the chromophore is chemically linked to the host polymer.

Once the difficulties are overcome, poling larger thicknesses of EO polymers will result in enhanced performance of EO devices in practical applications, such as those currently being investigated for THz generation. The thicker path length available in bulk-poled polymers will allow improved THz power, sensitivity, and signal-to-noise ratio in both THz generators and detectors. Large-area Pockels cells constructed from EO guest-host polymers will find new uses in high-speed modulators and shutters, and any application requiring a large d_{33} or r_{33} will potentially benefit from bulk-poled guest-host polymers and copolymers.

As a first step toward chemically linking the chromophore to the host polymer backbone, the use of ROMP for the synthesis of thermally stable EO polymers is explored. The initial studies indicate that tunable, high T_g EO polymers can be directly prepared in quantitative yields under undemanding reaction conditions. The polymers are soluble in common organic solvents and are readily processed in bulk. The U.S. Army Research Laboratory is in the process of measuring the EO properties of these polymers on both bulk and thin films.

5. References

1. Sinyukov, A.; Hayden, M. Generation and Detection of Terahertz Radiation With Multilayered Electro-Optic Polymer Films. *Optics Letters* **2002**, *27*, 55.
2. Sinyukov, A.; Hayden, M. Efficient Electro Optic Polymers for THz Applications. *J. Phys. Chem. B* **2004**, *108*, 8515.
3. Andzelm, J.; Rawlett, A.; Dougherty, J.; Govind, N.; Baer, R. Performance of DFT Methods in the Calculation of Optical Spectra of Chromophores. *Proceedings of the DoD HPCMP Users Group Conference*, Seattle, WA, 14–17 July 2008; pp 235–240.
4. Herman, W.; Hayden, W. Maker Fringes Revisited: Second-Harmonic Generation From Birefringent or Absorbing Materials. *JOSA B* **1995**, *12*, 416.
5. Nahata, A.; Shan, J.; Yardley, J. T.; Wu, C. Electro-Optic Determination of the Nonlinear-Optical Properties of a Covalently Functionalized Disperse Red 1 Copolymer. *JOSA B* **1993**, *10*, 1553.
6. Davey, M. H.; Lee, V. Y.; Wu, L. M.; Moylan, C. R.; Volksen, W.; Knoesen, A.; Miller, R. D.; Marks, T. J. Ultrahigh-Temperature Polymers for Second-Order Nonlinear Optics. Synthesis and Properties of Robust, Processable, Chromophore-Embedded Polyimides. *Chem. Mater.* **2000**, *12*, 1679.
7. Zhang, C.; Zhang, H.; Oh, M. C.; Dalton, L. R.; Steier, W. H. What the Ultimate Polymeric Electro-Optic Materials Will Be: Guest-Host, Crosslinked, or Side-Chain? *Proc. SPIE* **2003**, *4991*, 537.
8. Slugovc, C. The Ring Opening Metathesis Polymerisation Toolbox. *Macro. Rapid Commun.* **2004**, *25*, 1283.
9. Lambeth, R. H.; Moore, J. S. Light-Induced Shape Changes in Azobenzene Functionalized Polymers Prepared by Ring-Opening Metathesis Polymerization. *Macromolecules* **2007**, *40*, 1838.
10. Fox, T. G. Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Polymer System. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

NO. OF
COPIES ORGANIZATION

1 DEFENSE TECHNICAL
 (PDF INFORMATION CTR
 only) DTIC OCA
 8725 JOHN J KINGMAN RD
 STE 0944
 FORT BELVOIR VA 22060-6218

1 DIRECTOR
 US ARMY RESEARCH LAB
 IMNE ALC HRR
 2800 POWDER MILL RD
 ADELPHI MD 20783-1197

1 DIRECTOR
 US ARMY RESEARCH LAB
 RDRL CIM L
 2800 POWDER MILL RD
 ADELPHI MD 20783-1197

1 DIRECTOR
 US ARMY RESEARCH LAB
 RDRL CIM P
 2800 POWDER MILL RD
 ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

1 DIR USARL
 RDRL CIM G (BLDG 4600)

INTENTIONALLY LEFT BLANK.